DEVICE AND METHOD FOR NON-DISPERSIVE CONTACTING OF LIQUID-LIQUID REACTIVE SYSTEM

Field of the invention

The present invention relates to an improved method and device for non-dispersive contacting of liquid-liquid reactive system. In particular, the present invention relaxes to a process and an apparatus for separating impurities from a liquid by a non-dispersive contacting of liquid-liquid reactive systems, said liquids being immiscible with each other.

Background of the invention

There arc many impurities/contaminant present in the downstream hydrocarbon products like LPG, gasoline, naphtha, kerosene, diesel etc, from petroleum crude processing units. These contaminants appear in hydrocarbon products due to natural source or produce during passing through different processing stages. The impurities like napthenic acid m diesel, hydrogen sulfide, mercaptans and COS in gasoline, LPG, naphtha and kerosene obtained from different units are required to be removed to meet the desired specifications which are becoming more and more stringent In order to meet the environmental statutory regulation.

These hydrocarbons are treated with either caustic or amine solution or by both in a contactor. As will be apparent to a person skilled in the art, & contactor should ensure proper contacting of immiscible liquid- liquid system. Such contactors could be a packed column, tray column, mixing valve or static mixer depending on specific application. For example, for removing H_2S/mercaptan from hydrocarbon stream, mixing valve is used. In mixing valve, one phase gets dispersed into the other phase as droplets, at the expense of shear energy. In this process ratio of hydrocarbon and caustic phase is important for maintaining efficiency of the process. Such process is effective when the reaction of the impurities with the second liquid is very fast, However, such processes suffer carryover of the dispersed phase along with the continuous phase. All these processes generates certain degree of turbulence between the phases.

Contactors are also known in which minimum turbulence is generated in the contact zone, Such contactors are made of fibre bundles (US Patent Nos: 3,754, 377; 3,758,404; 3,839,487 and 5,904,849). la such contactors, a series of thin fibre strands are housed in a column. (US Patent: 3,758,404) describes such arrangement. Further improvement is claimed to have been achieved in US Pat. 3,992,156.

For certain application for e.g. removal of napthenic acid from diesel, above contactors other than fibre film contactor can not be used as turbulence of phases creates emulsion which is stabilized by the sodium naphthenate which acts like a surfactant. Sodium naphthenate is formed during reaction of caustic with napthenic acid. Conventional contactors e.g. mixing valve, static mixer* do not work due to emulsion formation. Even with fibre film contactor, using conventional distribution system, emulsification could not be avoided. Therefore, there U an urgent need for developing a novel distribution system to ensure that turbulence in the interface of caustic and hydrocarbons is avoided.

Napthenic acids are the main contributors to acidity of the diesel. The napthenic acids react with caustic according to the following equation.

$$R\text{-}COOH + NaOH \quad - \quad R\text{-}COONa + H_2O$$

The sulfur compounds as hydrogen sulfide and mercaptans react with caustic according to the equations as follows:

$$H_2S + NaOH \quad = \quad RSNa + H_2O$$

$$RSH + 2NaOH \quad = \quad Na_2S + 2H_2O$$

Depletion rate of impurities is controlled by mass transfer rate as reaction rate is very high.

The mass transfer rate of reacting species can be expressed as: R-(k)(AXAC) Where

k mass transfer coefficient,

A Interfacial area, -

AC concentration gradient

In conventional treating mechanism, devices such as mixing valves and static mixers create interfacial area by dispersive mixing, which generate droplets, To maximize the surface area from a given volume, considerable shear energy must be imparted to form as many small droplets as possible. Also droplet size has to be as small as possible. Small droplets, however, have the disadvantage of taking longer time to separate from the bulk phase. Consequently, a large separator is provided.

The Continuous Film Contactor is a static contacting device that produces non-dipersive contacting of the caustic and hydrocarbon phases and improves the removal of acidic/sulphidic impurities from hydrocarbon streams. This prevents emulsion formation and results in minimum caustic carry over and high utilization of caustic solution,

The contactor, containing fibers provides a large interfacial area, which increases the mass transfer rate. At the same time, the aqueous phase is constrained to the fibre material by" surface tension forming a film OQ each fibre that contacts, but never mixes with the hydrocarbon phase. Consequently, separation of phases becomes a simple and efficient step in the process.

The efficiency of the mass transfer of undesirable contaminants from hydrocarbon phase to aqueous phase depends on the distribution of both the liquid phases into the fibre packing. Also, packing of fibers and fibre holding arrangement play an important role. Packing of fibers should be in such a way that it is equally and evenly distributed across the cross section and throughout the column length, so that caustic and hydrocarbon in any portion of the column should not pass without seeing each other. The interracial area of mass transfer depends upon how the column is packed i.e., fibre diameter, number of fibers.

Objects of the invention

It is an object of the invention to a provide a distribution system for processing hydrocarbon containing naphthemic acid with caustic without forming emulsion.

It is another object of the present invention to enhance the performance of the distribution system by optimizing operating parameters e.g. temperature, caustic concentration etc.

It is yet another object the present invention to improve performance of contactor by ensuring complete wetting of fibers before hydrocarbon phase is introduced

It is still another object the present invention to provide a process for removal of impurities where it requires less tune from phase separation, less space, less energy and less operating cost and better product specification with respect to removal of contaminants/ impurities.

It still another object the present invention to provide an apparatus for carrying out the process of the present invention.

It still another object the present invention to provide a novel distribution system to ensure that turbulence in the interface of caustic and hydrocarbons is avoided.

As a whole the overall object of the present invention is to develop a novel process and mass transfer equipment which can be used for removal of undesirable contaminants/ impurities like, naphthenic acid, hydrogen sulphide and mercaptans etc. present in product hydrocarbon streams like LPO, gasoline, naphtha, diesel, kerosene etc.

Summary of invention

The present invention relates to a novel distribution system for hydrocarbon and caustic for contact in contactor containing fibers. The distribution system consists of two stages of distributor. This system allows complete wetting of the fibre with aqueous phase before hydrocarbon phase is introduced.

Detailed Description of the Present Invention

Accordingly, the present invention provides an apparatus for separating impurities from a liquid by a non-dispersive contacting of a liquid-liquid reactive systems, said liquids being immiscible with each other, which comprises a cylindrical column separated into a first stage and a second stage, a plurality of modules of packed metallic fibers mounted in the first stage of said column on a support, a first distributor provided in the first stage of the column for distributing a first liquid located above said support such that said first

liquid completely wets said fibers by capillary action and forms a film thereon, a second distributor fitted at a bottom portion of the second stage for distributing a second liquid containing impurities on to the metallic fibers, wherein said second liquid flow co-currently with said first liquid so that the impurities present in said second liquid react with said first liquid and dissolve therein and a separator connected to a bottom of said column for separating the first liquid and purified second liquid.

In an embodiment of the present invention, the first distributor separates the cylindrical column into a first stage and a second stage in addition to distributing the first liquid.

In another embodiment of the present invention, the packed metallic fibers comprises of fine wires packed in a single or multiple tubes in order to enable mass transfer and / or mass transfer with chemical reaction to take place.

In yet another embodiment of the present invention, said modules comprise of a plurality of tubes held inside a metallic shell, said shell being supported either on said separator or independently outside said separator.

In still another embodiment of the present invention, the modules are supported in said column at their upper ends.

In one more embodiment of the present invention, the modules are suspended from tie rods mounted in said first stage of said column and the metallic fibers are supported and looped around said tie rods.

In one another embodiment of the present invention, the metallic wires are packed in the form of sinusoidal wave so that inter fiber void space is uniformly maintained.

In a further embodiment of the present invention, the metallic fibers are chemically treated to enhance wettability.

In another embodiment of the present invention, the metallic fibers are made of materials selected from stainless steel, phosphorous bronze, glass fibers and plastic materials.

In yet another embodiment of the present invention, the metallic fibers are of the thickness of from 0.1 mm to 0.3 mm.

In still another embodiment of the present invention, the modules of metallic fibers comprise of multiple tubes with a cap on top in each tube said cap being provided with an orifice designed for specific flow range.

In one more embodiment of the present invention, the first distributor is provided with a plurality of holes whose diameter is equal to or greater than the diameter of the packed metallic fibers.

In one another embodiment of the present invention, the second distributor is provided with plurality of holes whose diameter is equal to or greater than the diameter of the packed metallic fibers and plurality of holes of smaller diameter which are placed adjacent to the holes whose diameter is equal to or greater than the diameter of the packed metallic fibers.

In a further embodiment of the present invention, the separator provided at the bottom of the column is optionally provided with heating coils.

The present invention also provides a process for separating impurities from a liquid by a non-dispersive contacting of liquid-liquid reactive systems which comprises distributing a first liquid over a support consisting of packed metallic fibers mounted in the first stage of a two stage liquid distributor so that the entire support is completely wetted by said first liquid by capillary action, said first liquid forming a film over said support, distributing separately, a second liquid containing impurities to be removed, said second liquid being immiscible with said first liquid and flowing co-currently to said first liquid so that the dissolved impurities in said second liquid react with the film forming first liquid and dissolve therein, allowing the two liquids to flow downward to a separator and collecting the pure second liquid and if desires, recycling said first liquid.

In an embodiment of the resent invention, the first liquid is selected from a caustic solution or amine solution or both and said second solution is a hydrocarbon stream.

In another embodiment of the present invention, the hydrocarbon stream is selected from LPG, gasoline, naphtha, kerosene and diesel.

In yet another embodiment of the present invention, the impurities present in the second liquid are naphthenic acid, hydrogen sulfide, mercaptans and COS.

The present invention also relates to holding of fibers in the distributor in a novel way as modules and each module Is separately irrigated with caustic. Holding of fibers is an integral part of the distributor.

The present invention also relates to optimization of process parameters for enhancing performance of distribution system and removal of naphthemic acid from hydrocarbon phase without formation of emulsion.

As a whole the present invention relates to the development of special nondispersive type mass transfer equipment and its internal components, Efficiency of the process depends on the efficiency of the equipments.

A new and improved equipment is provided for effective contact between two immiscible liquids to obtain efficient mass transfer with reaction. The increased surface area in CFC compared to conventional contacting device including mixing valve improves the mass transfer rates between the two phases.

Thus the present invention discloses an apparatus called Continuous Film Contactor (CFC) and a method for efficient contacting of immiscible liquid - liquid reactive system. It is an apparatus consisting of novel two stage liquid distributor which ensures smooth continuous film of liquid over support consisting of SS fibres arranged in a way such that capillary action of wetting liquid is ensured. Second liquid, distributed separately, flows co-currently and the dissolved component from this stream react with the film forming liquid and dissolves.

Alternatively dissolved Impurities from the aqueous phase may be extracted by the hydrocarbon phase. The distribution system allows minimum drag of the flowing liquid

over film liquid and no turbulence is generated, which may cause emulsification in certain processes. Disclosed is a process for enhancing performance of distribution and contactor system.

Continuous Film Contactor (CFC) is a static contacting device in which mass transfer occurs in a co current flow of liquid-liquid system through a column tightly packed with fine proprietary metallic fibre. It has wide applications in petroleum refinery for treatment and purification of the products obtained from main stream and also in other fluid handling" industries, It provides the flexibility to meet both today's and tomorrow's environmental regulations on sulphur and other contaminants.

The present invention relates to proprietary design of aqueous and hydrocarbon phase distributors (2-Stage), fibre holding arrangement, and as a whole design of complete system for removal of hydrogen sulphide, mercaptan and other contaminants sulphur compounds from LPG and similar hydrocarbon stream and neutralization of naphthenic acid in diesel and thiophenol from light cycle oil using aqueous caustic solution. The application is not limited to caustic-hydrocarbon contacting. The invention could be used for any liquid -liquid system such as hydrocarbon -amine solution of water.

Accordingly, the present invention provides a process for separating impurities from a liquid by a non-dispersive contacting of liquid-liquid reactive systems which comprises distributing a first liquid over a support consisting of packed metallic fibres mounted in the first stage of a two stage liquid distributor so that the entire support is completely wetted by said first liquid by capillary action, said first liquid forming a film over said support, distributing separately, a second liquid containing the impurities to.be removed, said second liquid being immiscible with said first liquid and flowing co-currently to said first liquid so that the dissolved impurities in said second liquid reacting with the film forming first liquid and dissolving therein, allowing the two liquids to flow downward to a separator and collecting the pure second liquid and if desired, recycling said first liquid

The present invention also provides apparatus for separating impurities from a liquid by a non-dispersive contacting of liquid-liquid reactive systems, said liquids being immiscible

with each other, which comprises a cylindrical column, a plurality of modules consisting of packed metallic fibres mounted in the first stage of said column on a support, a flrsi distributor for distributing a first liquid located above said support so that said first fluid completely wets said fibres by capillary action and forms a film thereon, a second distributor for distributing said second liquid containing said impurities fitted at the bottom of said support, said second liquid flowing co-curreatly -with said first liquid so that the impurities present in said second liquid react with said first liquid and dissolve therein, and a separator, connected to the bottom of said column for separating the first liquid and said purified second liquid. Brief description of the drawings

Fig.l represents the general assembly of Fibre Film Contactor with all accessories like distributor, fibre support etc, fitted on a separator vessel with inlet and outlet provision.

Fig.2 depicts the general assembly of liquid distributors for aqueous and organic phase (2-stage distributor), fibre support.

Fig.3A describes the details of the 1st. stage distributor and tube sheets.

Fig.3B describes the details of the 2^{nd}, stage distributor and tube sheets.

Fig 4 depicts the details of fibre support/ holder, rings, rods for fibre tie up.

Fig,5 represents the overall assembly of the column, sleeve, distributors and fibre holder.

Fig.6 depicts the overall arrangement of contactor and separator used in commercial plant. Detailed description

In fig. 1 C- 01 (6) is a vertical glass contactor consisting of treated SS fibers (7). Caustic and diesel are introduced into the contactor (6). Caustic is introduced through a distributor (5). Diesel is a continuous phase and introduced from the side. Caustic flows preferentially around SS fibers. The contactor (6) is located on top of a glass separator in which caustic and hydrocarbon phase separate.

In the present distribution system it was observed, that emulsion is formed at the point where caustic and diesel meet. The emulsion formation continues up to the separator (8) and does not separate at all. This creates carry over of diesel in caustic and caustic in diesel. The reason for emulsion formation is basically generation of turbulence at the interface. Hydrocarbon phase comes out from top of the separator (8) through hydrocarbon line (9) and contaminated caustic is taken out from the bottom of the separator (8) through line (10). Provision of electrical heating arrangement (11) is provided in the separator (8).

Subsequently, a novel distributor system consisting of two stages as shown in fig. 2 was developed. The distributor comprises of fibers held together as modules (13). Each module (13) is separately irrigated with caustic. Aqueous caustic solution enters through nozzle (15) and is distributed in the caustic distributor (14). Fibers (7) are supported from tie rods (22) and tie rods are fixed on the ring (21). Sufficient height is provided to allow complete wetting of the fibers with caustic. Details of caustic distributor is shown in fig.3 A. This is followed by distribution of diesel in the second distributor (19) located below caustic distributor. Diesel is fed to distributed uniformly such that no turbulence occurs. Since the fibers are already wetted with caustic, drag force created by diesel flow can not dislodge caustic from the fibers. At least two vents nozzles (16,18) are provided at two zones of distributor. Bach module (13) of fibers passes through tube sheet-A (20).

In the novel distribution system of the present invention, no emulsion formation was observed in any part of the contactor and separator, Process was further optimized by manipulating temperature of caustic & diesel, flow ratio of diesel and caustic.

The system of the present invention was used to evaluate the performance of the equipment. Different type of diesel of TAN value varies from 0,5 to 0.7 mg KOH/gm of diesel (Acidity due to naththenic acid content) have been tested for napthenic acid removal, product is obtained with TAN value of 0.025 to 0 087 mg KOH /gm of diesel, It was well below the maximum limit of 15 mg KOH /gm diesel of TAN value.

A new and improved equipment/ internals are tested for effective contact between two immiscible liquids to obtain efficient mass transfer with reaction. The increased surface area in CFC compared to conventional contacting device including mixing valve improves the mass transfer rates between the two phases. The continuous film contactor is cylindrical column (23,25) in which metallic fibers (7) are hanged by a support (12), up to inside of the separator (8) at the bottom of the contactor (23,25) (Fig.5,6). The aqueous phase distributor (14) is fitted at the top of the fibre holder/ support (12) and hydrocarbon phase distributor (19) is fitted at the bottom of the fibre support (Fig. 2). Initially, metallic fibers are wetted by passing aqueous caustic solution through distributor (14) from the top of the fibers, then hydrocarbon phase is fed separately through other distributor). The two phases flow down co-currently through the contactor (25,7) at thin films, the reaction occurs at the surface. The mass transfer of the reactants from the bulk phase to interface and the transfer of the products from the interface to the bulk phase are enhanced due to thinness of the films,' As both the phases flow down to the separator (8), they are separated there. The bottom aqueous phase is re-circulated by pump (24) and fed to 1st stage caustic distributor (14) through nozzle (15).

The present invention will now be described with reference to the following non-limiting Example.

Example 1:

The naphtheaic acid content of NO diesel (140-390 °C) is much higher (0.6 mg KOH/gm or 0.256 wt%) than the recommended limit (0.15 nag KOH/gm or 0.05 wtVo), The described embodiment is used in the general assembly (Pig. 1) for this experimentation. Caustic solution is fed from the top of the contactor through the distributor (Fig.2,3A) (14) and NG diesel is fed through hydrocarbon feed nozzle (1?) and distributed through hydrocarbon distributor (Fig.2,3B) (19). Thin layer ia formed on the fibre (7) surface with aqueous caustic solution and diesel passes downwards along the film co-currently. Purified diesel is withdrawn from the top phase k the separator (8). The TAN value of diesel was obtained as 0.022 to 0.087 mg KOH/gm or 0.286 wt% TAN value.

The different operating parameters were used for the process. These are as follows:

Optimum caustic concentration	0.5-3%
Caustic: Diesel flow ratio	1:10-1:20
Operating temperature	40 to 46° C
Distributor	2 Stage
Residence time in separator	10-30 mins.
Type of fibre	Stainless Steel
Treatment	Chemical
Shape	Sinusoidal

The experiment was repeated with a bigger size contactor in which re-circulation of caustic was maintained.

The caustic solution is pumped and filled in the separator (8). The caustic solution is then recycled from separator (8) and distributed over the top of the continuous Film Contactor through caustic distributor (Fig.2&3A). The hydrocarbon is pumped and distributed through hydrocarbon distributor (Fig.3B), where fibre bundle* (13) are supported from the top and hanged inside the sleeve (25) up to bottom of the separator (8). The caustic solution wets the fibres (7) preferentially and flows downwards to the bottom of the separator (8), The hydrocarbon also flows downward forming a layer around the caustic wetted fibres. The naphthenic acid present in hydrocarbon dissolve in the caustic phase around the fibres (7) in the contactor (25).

The treated hydrocarbon and caustic solution are separated in the separator (8). The caustic solution from separator (8) is recycled back to the contactor till the depletion of concentration of caustic solution below 2 wt%. Purified hydrocarbon is withdrawn from the top phase in the separator (8).